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RESEARCH AND DEVELOPMENT ON ADVANCED GRAPHITE MATERIALS

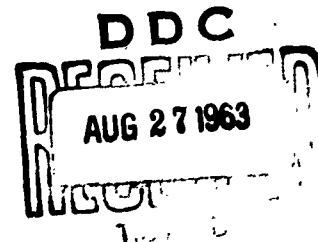
Volume XVI — An Electron Spin Resonance Study of
Thermal Decomposition Reactions of Organic Compounds

TECHNICAL DOCUMENTARY REPORT No. WADD TR 61-72, VOL. XVI

JUNE 1963

AF MATERIALS LABORATORY
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735002
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Project No. 7-817



(Prepared under Contract No. AF 33(616)-6915
by the Research Laboratory, National Carbon Company,
Division of Union Carbide Corporation, Parma 30, Ohio;
L. S. Singer and I. C. Lewis, authors.)

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FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials", Task No. 735002 "Graphite Materials Development"; Project No. 7381 "Materials Application", Task No. 738102 "Materials Preproduction Process Development"; and Project No. 7-817 "Process Development for Graphite Materials". The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acting as Project Engineers.

Work under this contract has been in progress since May 1, 1960. The work covered in this report was conducted at the Research Laboratory of the National Carbon Company located at Parma 30, Ohio, under the direction of J. C. Bowman, Director of Research, and W. P. Eatherly, Assistant Director of Research.

The authors would like to thank Dr. H. J. Bowlden for programming and carrying out the HMO calculations and Miss S. L. Bushong for synthesizing the diazo compounds.

Prior reports issued under USAF Contract AF 33(616)-6915 have included:

WADD Technical Notes 61-18 and 61-18, Part II, progress reports covering work from the start of the Contract on May 1, 1960 to October 15, 1961, and the following volumes of WADD Technical Report 61-72 covering various subject phases of the work:

- | | |
|------------|--|
| Volume I | Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague. |
| Volume II | Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence. |
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- Volume VIII** **Electron Spin Resonance in Polycrystalline Graphite,**
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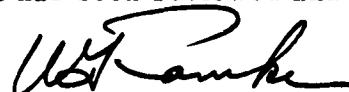
ABSTRACT

Initial results of an ESR (electron spin resonance) survey of the thermal decomposition and carbonization of pure organic compounds are presented. ESR measurements were performed during pyrolysis in inert polyphenyl solvents to permit the observation of resolved hyperfine structure of radical intermediates. The generality of radical formation during carbonization is demonstrated.

Detailed investigations have been made on the model aromatic hydrocarbons, acenaphthylene, 9,9'-bifluorenyl and 9,9'-bifluorylidene which provide examples of extremes in graphitization behavior. Results are discussed in terms of reaction mechanisms and the nature of radicals in low temperature carbons. Resolved spectra for acenaphthylene and two deuterated analogs are compared. Possible structures for the observed radicals from both acenaphthylene and the bifluorenyl-bifluorylidene system are presented and discussed theoretically in terms of the H. M. O. (Hückel Molecular Orbital) method.

ESR studies are also reported for the thermal decomposition of several aromatic diazocompounds. The observed stable radical intermediates are believed to result from further reaction of the initially generated carbene species. Detailed studies of the decomposition of diphenyl diazomethane suggest the presence of a radical intermediate containing the $\phi_2\dot{C}-N\angle$ grouping.

This technical documentary report has been reviewed and is approved.



W. G. RAMKE

Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

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1. INTRODUCTION

This report describes the first phase of an electron spin resonance (ESR) study of thermal decomposition and carbonization reactions of organic compounds. The goal of this project is to elucidate the mechanisms of the initial chemical reactions of carbonization. An understanding of these reactions will certainly clarify the relations between the microscopic structure of carbons and the nature of the starting material.

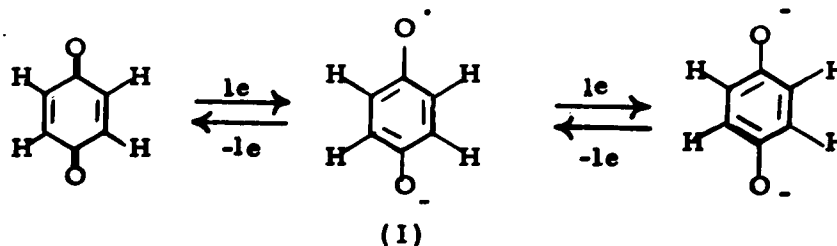
At present, there exists an extensive literature (~ 100 papers) on the application of the ESR technique to the study of charred materials and the carbonization process.⁽¹⁾ However, since these studies were all made on inhomogeneous solid systems, the ESR consisted of a single line devoid of resolved structure and almost devoid of information. Interpretation was therefore limited to a phenomenological and qualitative description of carbonization as a bond breaking and aromatization process resulting in the formation of large aromatic organic free radicals. The precise structures of the radicals observed in large concentrations had never been determined, although their importance as chemical intermediates in the carbonization process had been suspected.

It was this unsatisfactory state of affairs which led us to perhaps the most important single result of this study to date. We have found that thermal decomposition including carbonization reactions can be carried out in inert liquid solvents and the ESR observed simultaneously in situ. The use of such liquid systems has the following consequences.

1. The free radicals which are formed in the liquid phase are free to tumble rapidly. This rapid molecular motion effectively averages out anisotropic nuclear hyperfine interactions and permits the observation of a well-resolved ESR spectrum. Such a spectrum is required for the identification of the radicals.
2. Since the solution of a carbonizable material in an inert solvent constitutes a homogeneous system, the different paths and rates of the various reactions can be altered and studied in a controlled manner by varying concentration, temperature and other experimental parameters.
3. The in situ ESR experiment, which is carried out in a specially designed heater cavity, has the advantage of enabling the course of a free radical reaction to be followed as it occurs.

It may be worthwhile giving just a few examples of the way in which ESR has been used in other more tractable chemical systems for the identification of radicals and the elucidation of reaction mechanisms. The quinone - semiquinone reactions, first studied by Fraenkel and coworkers, have become classic examples of the way in which ESR can prove the identity of a radical intermediate.⁽²⁾ In benzo-semiquinone anion (I), which is a radical intermediate in the reduction of benzoquinone to hydroquinone in alkaline solution, the unpaired

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electron is delocalized to a considerable degree. Since the molecule contains 4 equivalent protons, there are 5 magnetically nonequivalent arrangements of the 4 proton magnetic moments (each proton can be either spin up or down). The 5 slightly different local magnetic fields produce a small splitting of the electron spin energy levels giving rise to a nuclear hyperfine structure (hfs) in the ESR. It can be shown that n equivalent protons will give rise to a hfs with $(n + 1)$ equally spaced resonance lines having an intensity distribution given by the ratios of coefficients in the binomial expansion of $(n + 1)$.⁽³⁾ The magnitudes of the hfs splittings are proportional to the electron densities at the various nuclei. It is thus often possible not only to identify the number of groups of equivalent protons in a free radical, but also to determine quantitatively the odd electron distribution in the molecule.

Weissman and coworkers⁽⁴⁾ have pioneered in the application of ESR to the study of the hfs of aromatic mononegative and monopositive ions. For simple molecules such as anthracene, the Hückel approximation to the molecular orbital theory (HMO theory) provides quantitative agreement between the predicted spin densities and the experimentally observed hfs.⁽⁵⁾ Since most of the systems with which this report is concerned are π -electron systems (aromatic organics), Weissman's work and the application of HMO and valence bond theories are particularly relevant.

Abell and Piette⁽⁶⁾ have identified by ESR the highly unstable radical intermediates during the addition of hydrogen bromide to olefins at low temperatures. The hfs also yielded information about the conformation of the radical intermediates and the resultant brominated products.

The present report includes a brief description of the experimental techniques in Section 2. In Sections 3 and 4, the carbonization of organics is discussed, including both a qualitative survey and the more quantitative studies of the acenaphthylene and bifuorenyl-bifuorylidene systems. The work on the thermal decomposition of diazo compounds is presented in Section 5.

2. EXPERIMENTAL

2.1. ESR Measurements

The experiments were carried out in a conventional ESR spectrometer at about 9.5 Gc/sec.⁽⁷⁾ A photograph of the magnet and associated

microwave equipment is shown in Figure 1. In order to avoid saturation and retain high sensitivity, superheterodyne detection was employed at microwave powers less than 100 microwatts. Magnetic field modulation at 280 cps was used.



N-244

Figure 1. Electron Spin Resonance Apparatus

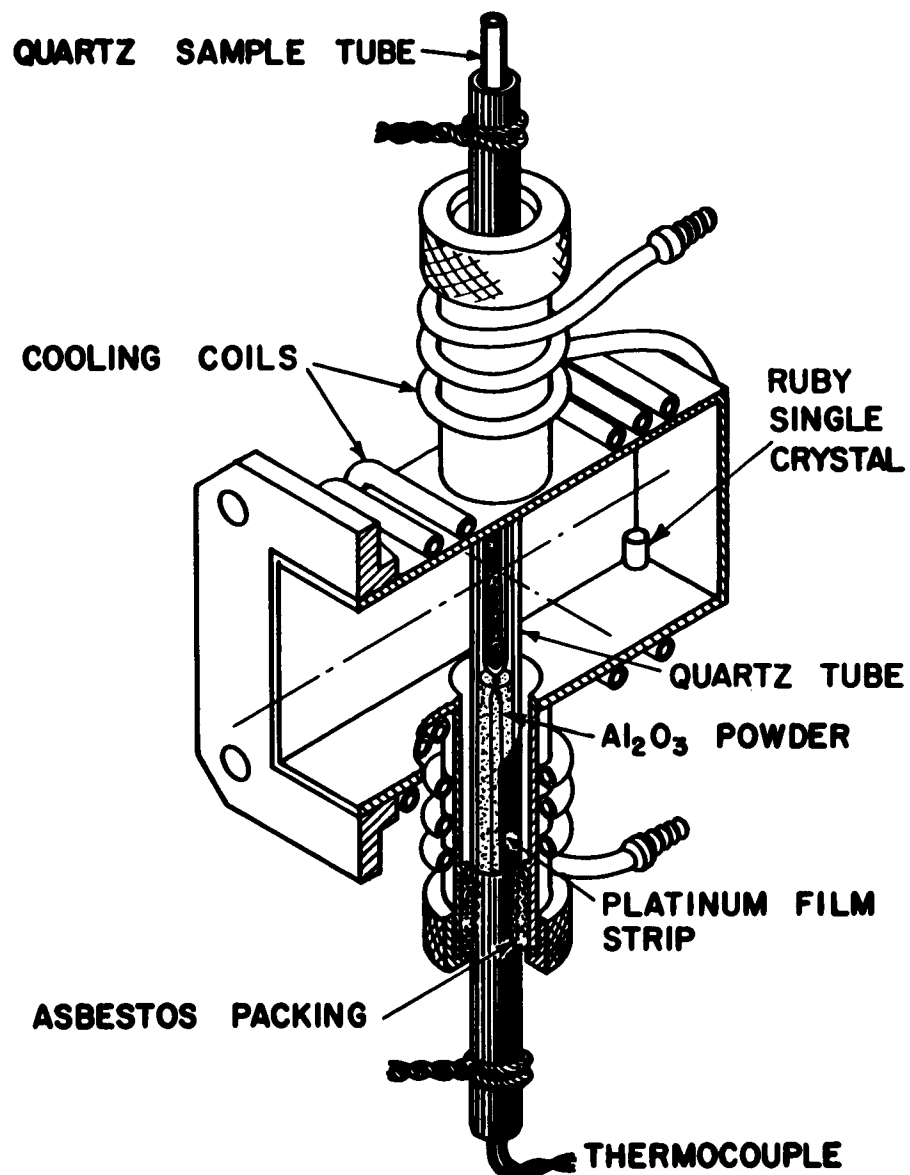
Experiments were performed in the Varian "100 kc" cavity at temperatures up to about 300°C. Carbonization and higher-temperature experiments were performed in the heater cavity shown in Figure 2.⁽⁸⁾

2.2. Sample Preparation

Samples were prepared as solid mixtures of the particular compound to be studied and the appropriate polyphenyl solvent. The solid mixtures were introduced into 5 mm o.d. Pyrex tubes which were then evacuated and sealed under vacuum.

2.3. Materials

1. Solvents -- m-Quinquephenyl was obtained from Aldrich Chemical Company and was either employed as-received or recrystallized from ethanol. The liquid range of this hydrocarbon (125-540°C) makes it a convenient solvent for carbonization studies. Biphenyl was E.K. Co. White Label Grade.



N-4004

Figure 2. Heater Cavity

2. Aromatic Compounds -- All aromatic compounds employed in carbonization studies were obtained from commercial sources and either used as-received or purified by recrystallization.
3. Diazocompounds -- The diazocompounds reported herein were prepared by standard methods from the corresponding hydrazones.⁽⁹⁾

3. ESR DURING CARBONIZATION OF ORGANIC COMPOUNDS -- GENERAL SURVEY

In order to determine the generality of the occurrence of radical intermediates during carbonization, a survey was made of the ESR of a variety of carbonizable organic compounds during the early stages of pyrolysis. Included were aromatic hydrocarbons, substituted aromatics, polymers, and one aromatic hydrocarbon-quinone mixture. The initial pyrolysis was accomplished either in an external furnace with subsequent transfer to the heater cavity or by direct heating in the heater cavity.

Compiled in Table 1 are the compounds which we have studied to date. The heat-treatment temperature and the temperature of measurement in parentheses are given in the second column. The solvent and concentration are listed in column three and the spectrum reference number in column four. Finally, in the last column, the observation of a resolved (R) or unresolved (U) spectrum is indicated.

The observation of ESR during the initial stages of pyrolysis for every carbonizable material which we have examined to date demonstrates the generality of radical intermediates in the carbonization process. In many instances only broad unresolved spectra rather than resolved hfs were obtained. Such an unresolved spectrum is generally observed for complex low temperature chars and pitches.⁽¹⁾ In all cases the spectral line widths were approximately 10 gauss and the g-values were approximately equal to the free electron value. It is not yet clear whether the lack of hfs in these instances is due to experimental variables such as low solubility and incomplete removal of atmospheric oxygen or are inherent with the systems.

Ideally, the measurement of a completely resolved hyperfine spectrum should permit identification of the respective radical intermediate. This identification is generally accomplished by the comparison of a theoretically derived spectrum with that measured experimentally. For many of the aromatic structures in this study, theoretical spectra must be based either on a relatively simple Hückel molecular orbital treatment of the molecule in question or by the use of more complex quantum mechanical methods. Continuing effort is therefore being directed both along the lines of obtaining completely resolved ESR spectra during carbonization and comparing these spectra with those derived theoretically for the likely radical intermediates.

Table 1. General ESR Survey of the Carbonization of Organic Compounds

Compound	Temp. °C (a)	Solvent (e)	Curve No.	Spectrum Resolved (R) Unresolved (U)
9-Bromofluorene	260	None	2769-71	U
9, 10-Dibromofluorene	250	None	2763-8	U
Δ 10, 10'-Bianthrone	138	20:1 m_s	2872	R
4, 4'-Dimethyl- Δ 10, 10'- Bianthrone	260	20:1 m_s	2873-5	R
9, 10-Dimethyl anthracene	500	10:1 m_s	2568-70	U
4, H-Cyclopenta(d, e, f)phenan- threne	500 (150)	20:1 m_s	2681-2	R
Polyvinyl Chloride	500 (150)	20:1 m_s	2686-8	R
1:1 Anthracene-Chloranil	200	10:1 m_s	2703, 2711-12	R
9, 10-Dibenzyl anthracene	500 (175)	20:1 m_s	2678-9	R
2, 2'-Azonaphthalene	500 (150)	20:1 m_s	2683	U
9-Benzylidene fluorene	500 (150)	20:1 m_s	2680	U
Naphthacene	500 (150)	20:1 m_s	2641-2, 2677	U
Pentacene	500 (150)	20:1 m_s	2643-4	U
7, 12-Dimethyl benz(a) anthracene	500 (150)	20:1 m_s	2646-8	U
Acenaphthylene	400-500 (b)	(b) m_s	(b)	R
9, 9'-Bifluorenyl	400 (c)	(c)	(c)	R
9, 9'-Bifluorylidene	400 (c)	(c)	(c)	R
m-Quinquephenyl	> 540 (d)	(150) None	2682	U
Polydivinyl Benzene	500	10:1 m_s	2649-50	U
α -Truxene	500	10:1 m_s	2645	U

(a) When a single temperature is given, the temperature of decomposition and measurement are the same. In other cases, the temperature in parenthesis is that for spectrum measurement.

(b) Conditions of measurements given in Section 4.1.

(c) Conditions of measurements given in Section 4.2.

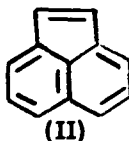
(d) Resonance observed only after prolonged heating at high temperatures.

(e) 20:1 m_s denotes 20 parts of m_s to one part of the carbonizable material; m_s is an abbreviation for meta-quinquephenyl.

4. DETAILED STUDIES OF THE MODEL AROMATICS ACENAPHTHYLENE AND BIFLUORENYL-BIFLUORYLIDENE

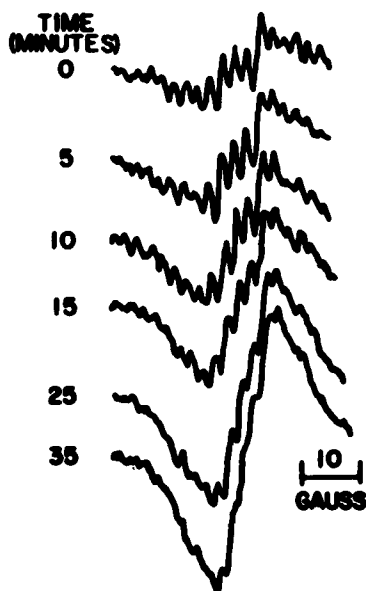
More detailed ESR investigations have been directed toward two organic systems, acenaphthylene and bifluorenyl-bifluorylidene. These three compounds all yield resolved hfs spectra(cf. Table 1). Furthermore, these systems are ideal models for the study of carbonization since they represent the extremes in graphitization behavior. Acenaphthylene, after carbonization can be thermally converted to an extremely ordered graphitic structure. On the other hand, bifluorenyl and bifluorylidene both yield essentially poorly graphitizable carbons. The thermal chemical transformations of these compounds have been recently discussed. (10)

4.1. Acenaphthylene



The ESR study of the initial pyrolysis of acenaphthylene (II) is of interest not only for establishing the nature of radical intermediates in this particular process but also for clarifying the role of radicals in carbonization in general.

Shown in Figure 3 is a series of curves for a 1:10 solution of acenaphthylene in the inert diluent m-quinquephenyl measured at 420°C. In this experiment the evacuated sample tube was gradually subjected to increasing temperature until the first signal appeared. The signal shown at the top of Figure 3 consists almost entirely of the resolved hyperfine spectrum (hfs). At 420°C the intensity of the hfs is seen to remain roughly unaltered for the first 15 minutes while the broad background signal (~ 10 gauss wide) commences to grow. After 15 minutes the hfs has essentially disappeared leaving only a broad resonance signal.



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Figure 3. ESR Curves for a 1:10 Solution of Acenaphthylene in m-Quinquephenyl at 420°C.

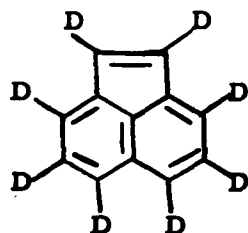
A reasonable explanation of this behavior is as follows. The hfs is due to the first free radical intermediate formed by the decomposition of the acenaphthylene polymer moiety. ⁽¹⁰⁾ Initially, a steady-state situation ensues in which the rates of formation and disappearance of the intermediate radicals are equal. The initial radicals can disappear by combining with other radicals or molecules to form larger more complex species of both radical and non-radical nature. After the first radical stage, many reaction paths are available for the formed intermediate. Further reactions lead to a complex mixture of aromatic radicals each possessing a complicated structure with many nonequivalent protons. A resolved hfs thus becomes impossible and only a broad signal is recorded at this "pitch" or more advanced carbonization stage.

The lifetime of each molecule of radical intermediate must be fairly long (a millisecond or longer) since saturation measurements indicate that T_1 is about that long. The ~ 1 gauss hyperfine component linewidths are therefore not lifetime limited. The further resolution of these lines therefore seemed likely.

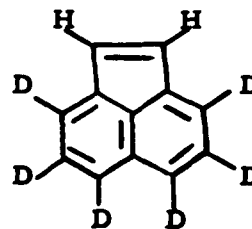
Shown in Figure 4 is a series of ESR curves for another 1:10 acenaphthylene m-quinquephenyl mixture heated for a short interval at 450°C and then observed at several lower temperatures. The solid material run at room temperature shows no hfs at all as would be expected for a randomly oriented polycrystalline material. Although substantial saturation was observed for the solid at powers above 100 μ watts, no hfs could be observed even at lower microwave power. At 90°C which is close to the melting point of the solution, motional averaging of the anisotropic hfs becomes apparent and at 168°C, the hfs lines become better resolved. At this temperature, the ESR spectrum does not change with time which indicates that the radicals formed at high temperatures have been essentially quenched.

If the temperature is raised to $\sim 320^\circ\text{C}$, it is found that both the hfs and the broad component slowly decrease with time. Apparently this temperature is too low to create new radical species but is high enough to cause the combination of radical entities into diamagnetic products. These results indicate that further reactions of the radical intermediates can yield both more complex aromatic radicals and larger diamagnetic aromatic hydrocarbons.

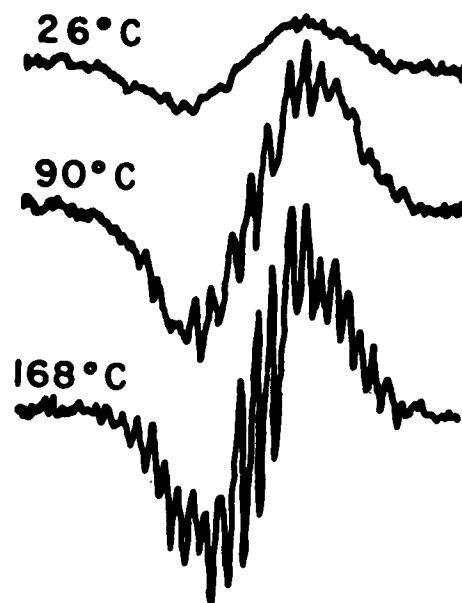
In Figure 5 are shown a series of ESR curves obtained for acenaphthylene and two deuterated analogs, D_8 -acenaphthylene and 2, 3, 4, 5, 6, 7- D_6 -acenaphthylene under identical conditions.



D_8 -Acenaphthylene
(III)

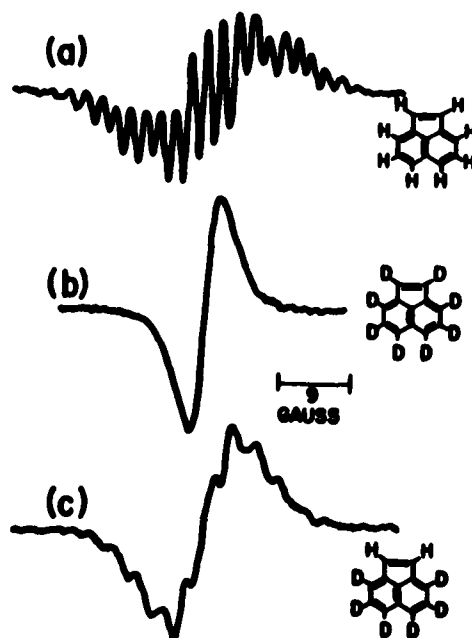


2, 3, 4, 5, 6, 7, - D_6 -Acenaphthylene
(IV)



N-2660

Figure 4. ESR Curves at 10μ Watts for a 1:10 Solution of Acenaphthylene in m-Quinquephenyl; Sample Heat-Treated Previously for Short Time at 450°C



N-3974

Figure 5. Comparison of ESR of Acenaphthylene and its Deuterated Analogs; 1:10 Solutions in m-Quinquephenyl Heated at 450°C , Measured at 160°C

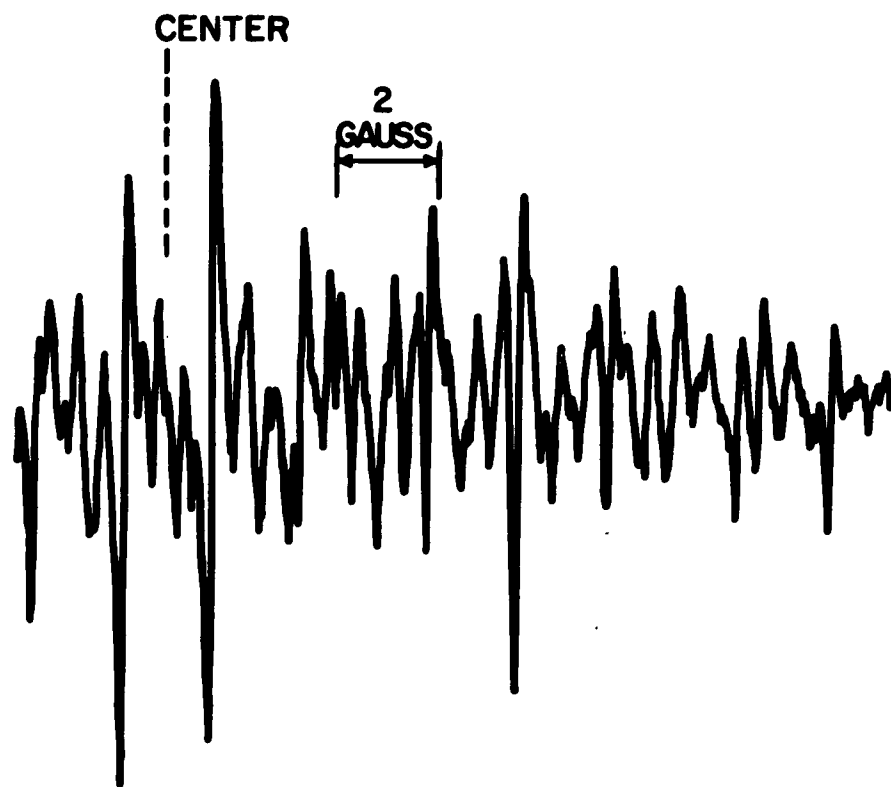
The second curve for the completely deuterated material exhibits a single sharp line. The entire spectrum has collapsed to about $\frac{1}{3}$ the width of the spectrum for the protonated material. This result is expected for the decrease in the hyperfine interaction in going from H to D. The third curve for the partially deuterated isomer shows a partial collapse intermediate to the above two cases. The isotope effect demonstrates that most but not all of the unpaired spin density is in the deuterated aromatic ring system. The observation of 3 main peaks in this spectrum implies an interaction with 2 equivalent protons. However, the situation is more complex since the appearance of several additional satellite peaks may indicate an interaction of the unpaired electron with other protons.

The series of curves in Figure 5 also provides good evidence that the relatively broad signals (~ 10 gauss wide) observed in very low temperature chars and pitches result from the cumulative hyperfine interactions between the unpaired electron and protons in the various ring systems.

Subsequent improvement of experimental techniques permitted the measurement of the acenaphthylene spectrum under conditions of high resolution. Using a magnetic field modulation of 0.2 gauss and a lock-in amplifier time constant of $\frac{1}{2}$ second, the sharp-line spectrum in Figure 6 was observed. The spectrum appears completely different from the previous incompletely resolved spectra in Figure 4. Many more lines with linewidths of 0.1 gauss or less are present. Actually, only a portion of the symmetrical spectrum is shown.

The complexity of this spectrum precludes any simple analysis. In view of the many overlapping lines, an improvement in experimental conditions will be required for obtaining the resolution necessary for an unambiguous assignment of the spectral lines. However, the present data can still serve as a useful qualitative guide for determining the structure of the acenaphthylene radical intermediate. The spectrum of the D_4 -acenaphthylene in Figure 5, which exhibits 3 large lines in the center in a 1:2:1 intensity ratio, indicates the presence of 2 equivalent protons outside the naphthalenic ring system. The splitting constants for these protons are fairly large, $a \approx 2.6$ gauss. The two large lines close to the center of the acenaphthylene spectrum in Figure 6 suggest but do not prove the existence of a splitting by a single proton. This splitting (~ 1.6 gauss) might not be observable in the poorly resolved D_4 -acenaphthylene spectrum.

A likely possibility for the structure of this radical is shown in Figure 7 which outlines our present view of the initial stages of pyrolysis of acenaphthylene. The first radical intermediate is believed to be involved either in the thermal breakdown of the initially formed acenaphthylene polymer (V) or in the subsequent rearrangement to the zethrene-type structure, (VIII) or (IX).

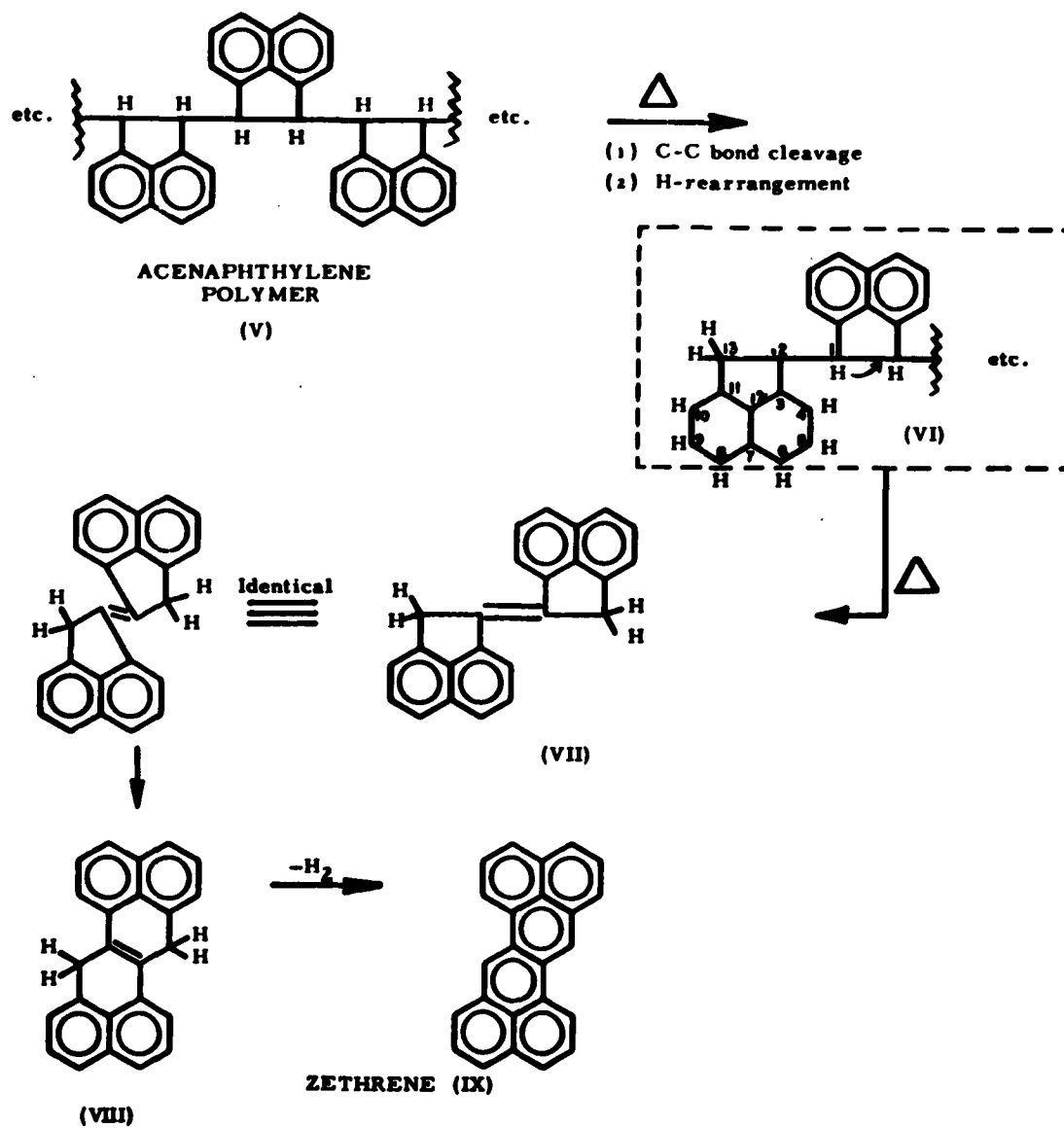


N-3442

Figure 6. Portion of ESR Spectrum of Thermally Decomposed Acenaphthylene Under Conditions of High Resolution

The proposed radical (VI) is at the end of a polymer chain and would be formed by thermal breakup of the polymer (V) and a subsequent hydrogen rearrangement. The extensive hydrogen migration in the acenaphthylene pyrolysis and the evidence for formation of reactive dimer units (VII) has been discussed elsewhere. ⁽¹⁰⁾

The π -system for the radical (VI) consists of carbons 2 through 12 and corresponds to an odd-alternate radical structure. The HMO calculation for this radical is quite straightforward in predicting the following spin densities at each position: $C_2 = 0.45$, $C_4 = C_6 = 0.20$, $C_8 = C_{10} = C_{12} = 0.05$, and $C_3 = C_5 = C_7 = C_9 = C_{11} = 0$. The hyperfine interaction of the two equivalent protons on carbon 13 and the proton on carbon 1 occurs by hyperconjugation and can only be estimated. The system should therefore be described by 4 coupling constants, a_1 for the single proton, a_{13} for the two protons on carbon 13, $a_{4,6}$ for the 2 protons on C_4 and C_6 and $a_{8,10}$ for the 2 protons on C_8 and C_{10} .

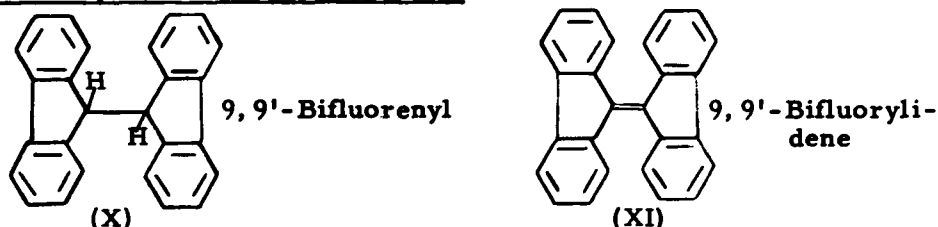


N-3446

Figure 7. Mechanism for the Formation of Zethrene from Acenaphthylene Involving Free Radical Intermediate

A total of $2 \times 3 \times 3 \times 3 = 54$ lines would be predicted which is less than the number actually observed. However, it should be pointed out that the simple HMO theory is frequently inadequate for quantitatively predicting spin densities. Therefore, the appearance of more than 54 lines does not necessarily exclude the proposed structure for the radical. Unambiguous identification of the radical will depend on the experimental determination of the coupling constants for a spectrum better resolved than that shown in Figure 6.

4.2. 9,9'-Bifluorenyl and 9,9'-Bifluorylidene



The related hydrocarbons, 9,9'-bifluorenyl and 9,9'-bifluorylidene, in contrast to acenaphthylene, yield very poorly graphitic materials on pyrolysis. It is of interest to attempt to relate this different graphitization behavior to the radical formation in the initial carbonization steps.

Both compounds yield resolved hyperfine spectra when heated to about 400°C in the diluent m-quinquephenyl. Under medium resolution the spectra appear identical except for slightly broadened lines for the bifluorylidene radical. The spectrum of six evenly spaced lines obtained for the bifluorenyl radical is reproduced in Figure 8.

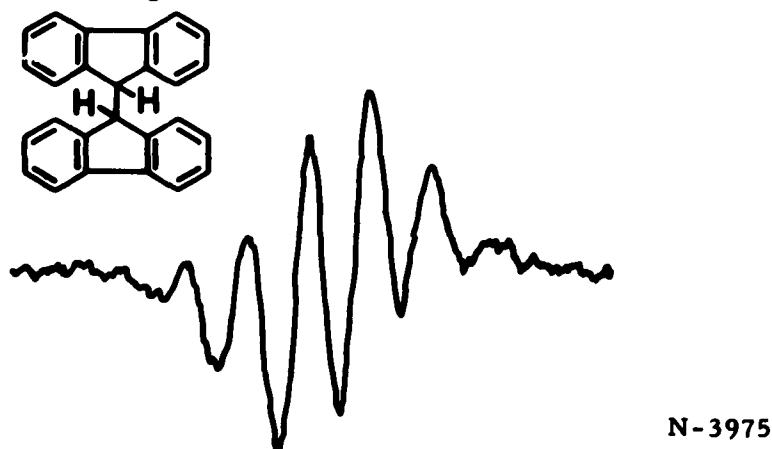


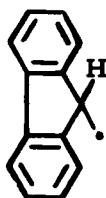
Figure 8. ESR Curve for a 1:10 Solution of 9,9'-Bifluorenyl in m-Quinquephenyl; Heated and Measured at 440°C

Both the bifluorenyl and bifluorylidene radicals exhibit similar temperature dependencies. The signals increase in intensity with increasing temperature without observable changes in line widths of the hyperfine

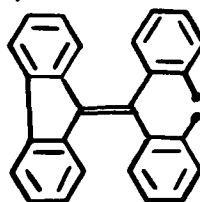
components. These effects appear reversible within specific temperature limits. Below $\sim 270^{\circ}\text{C}$, no hfs is observed whereas above 450°C , a broad "char" resonance similar to that shown in Figure 3 for acenaphthylene, begins to develop.

Under conditions of higher resolution, the simple six line patterns for both radicals can be resolved further to yield more complex fine-line spectra. The total number of lines, however, appears considerably smaller than that obtained for the acenaphthylene radical entity. These results are consistent with the graphitization behavior discussed earlier. Acenaphthylene would be expected to produce large planar aromatic radical intermediates and consequently a complex hfs. The simple spectra from the bifluorenyl-bifluorylidene systems could be attributed to the formation of less planar, smaller aromatic radicals which then would undergo combinations to yield nonplanar products.

The chemistry of the thermal transformation of bifluorenyl and bifluorylidene has been recorded elsewhere.⁽¹⁰⁾ Since the bifluorenyl undergoes thermal dehydrogenation to yield bifluorylidene, it is not yet clear whether the radical intermediates obtained from both compounds actually differ. The most likely structural intermediates are either fluorene-type radicals (XII) or biradicals such as (XIII).

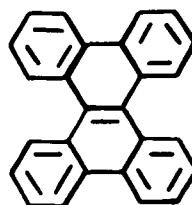


(XII)



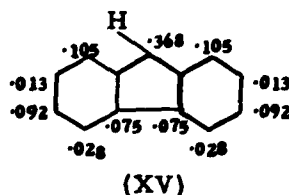
(XIII)

Formation of radicals of the type (XII) and (XIII) would be expected since the rearranged product tetrabenzonaphthalene (XIV) is produced in substantial amounts during pyrolysis.



(XIV)

The fluorene radical (XII) is a nonalternant neutral radical. An HMO calculation for this structure gives the spin density parameters as follows.

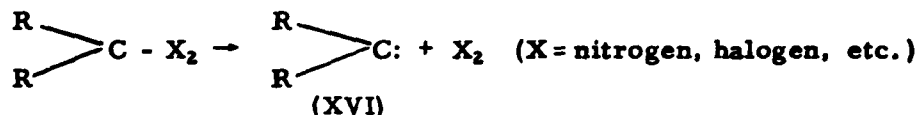


The calculation, which involved the diagonalization of a 13 x 13 matrix, was performed on a Royal Precision RPC-4000 computer. A valence bond calculation which may be more valid, is also being obtained for this species.

5. THERMAL DECOMPOSITION OF DIAZO COMPOUNDS

Carbonization is probably the most complicated type of thermal decomposition reaction. It seems reasonable that studies of several simpler thermal reactions involving radical intermediates, would help in interpreting complex carbonization phenomena.

Currently, perhaps the most extensively studied kind of thermal decomposition reaction involves the formation of divalent carbon intermediates. In fact, the entire area of organic research on divalent carbon is now designated as "carbene chemistry".⁽¹²⁾ An example of carbene formation is:



The ESR observation of the highly reactive carbene (XVI) has only recently been reported from studies on the irradiation of diphenyl diazomethane at liquid nitrogen temperatures.⁽¹³⁾

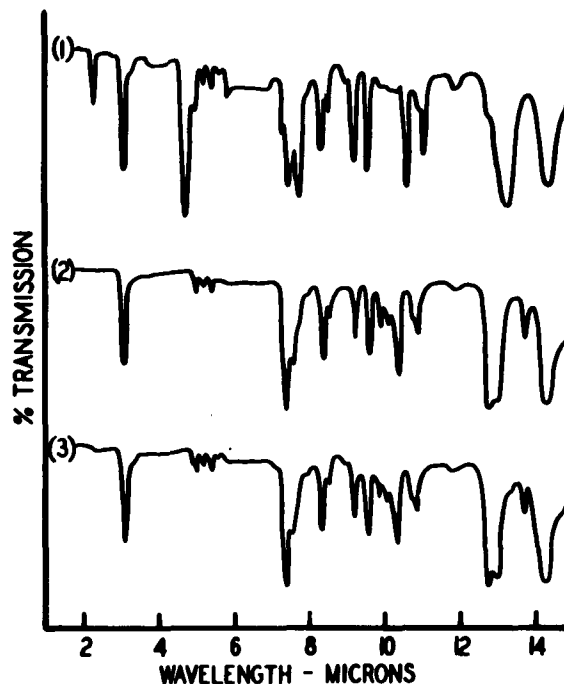
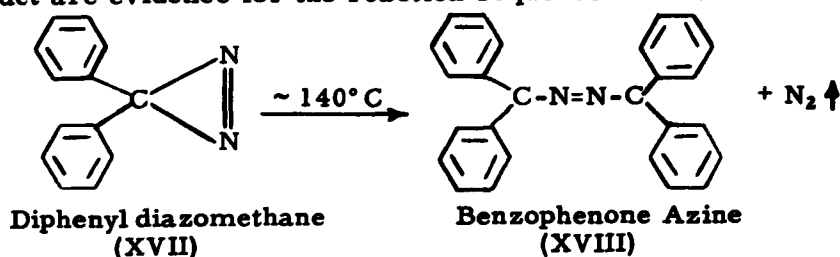
The discussion to follow describes our investigations of several diazo (X = nitrogen) thermal decompositions. The ESR experiments were carried out on solutions of the diazo compounds in polyphenyl solvents. The heater arrangement is identical to that described in Section 2.

5.1. Diphenyl diazomethane

The simplest known aromatic diazocompound is diphenyl diazomethane (XVII). Our investigations show that the major thermal transformation for this compound is the formation of the azine at a temperature of about 140°C.

Shown in Figure 9 are the infrared spectra of (XVII) curve (1), the reaction product from (XVII) at 140°C, curve (2), and finally that for the pure benzophenone azine, curve (3), synthesized by an independent means.⁽¹⁴⁾

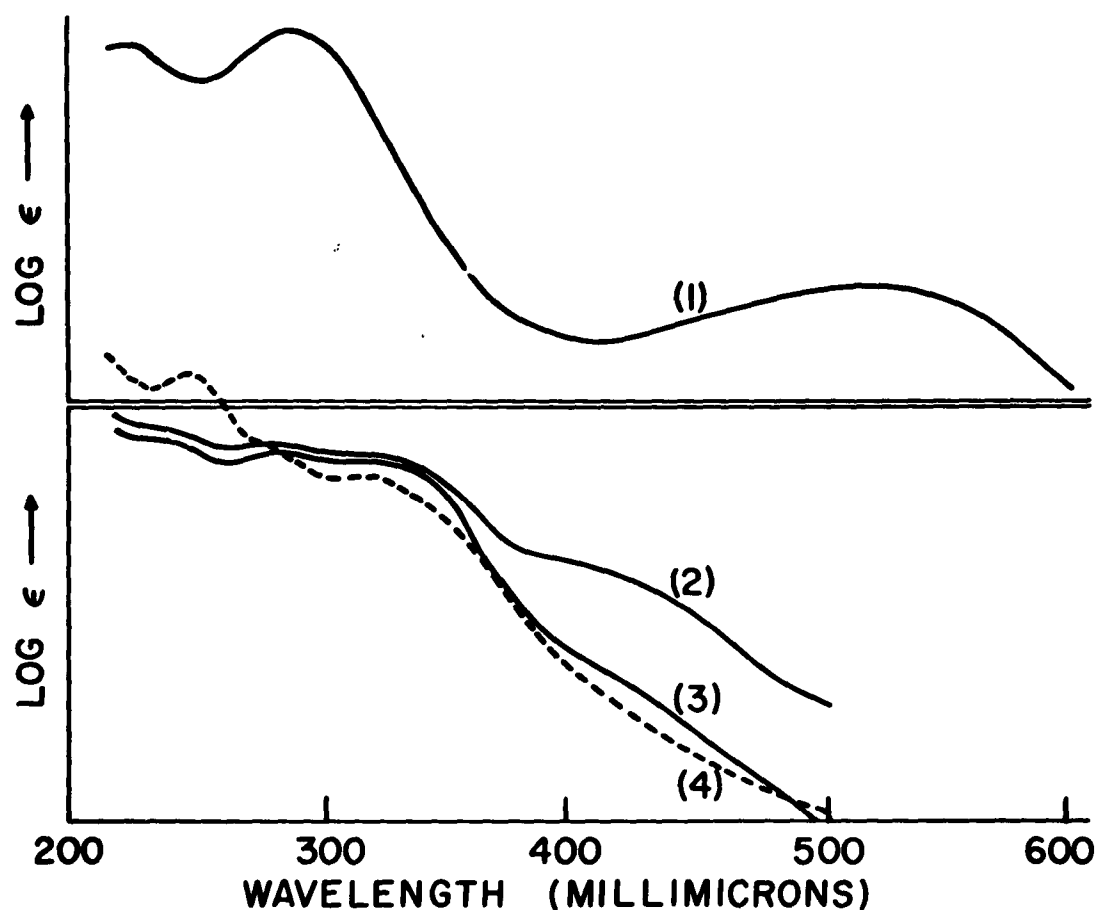
The identity of the last two spectra plus the general properties of the pyrolysis product are evidence for the reaction sequence below.



N-3976

Figure 9. Infrared Spectra for CS₂ Solutions of Diphenyl diazomethane and its Thermal Decomposition Products; (1) Diphenyl diazomethane, (2) Pyrolysis Product at 140°C, and (3) Benzophenone Azine

Given in Figure 10 are UV spectral curves for the same materials. Of special interest is the spectrum of the pyrolysis product. This spectrum (2) shows, in addition to the benzophenone azine bands, a broad absorption band at about 400 mμ. This band can be attributed to the yellow material which we have observed during the ESR measurements and which is believed to be the radical intermediate. Also displayed in Figure 10 is the spectrum of the decomposition product from UV irradiation of XVII, curve (4). This spectrum is essentially identical to that of the azine (3) and contains no additional bands in the visible region. This result is consistent with our observation that UV irradiation destroys the thermally formed radical intermediates. The additional absorption in the extreme UV in curve (4) is due to a small amount of benzophenone produced by the irradiation of the radicals in air.



N-3977

Figure 10. UV Spectra for Cyclohexane Solutions of Diphenyl diazomethane and its Reaction Products (1) Diphenyl diazomethane, (2) Pyrolysis Product at 140°C, (3) Benzophenone Azine, and (4) UV Irradiation Product at 25°C

The major reaction path is presumed to involve decomposition of (XVII) to yield the intermediate carbene which undergoes rapid combination with the parent diazocompound. The product benzophenone azine is found to be completely stable under the conditions of reaction.

The ESR behavior is as follows: at the reaction temperature of ~ 140°C, the incompletely resolved spectrum in Figure 11 is first observed. After a short time the spectrum changes to the symmetrical 23-line pattern in Figure 12a, which persists for several hours.

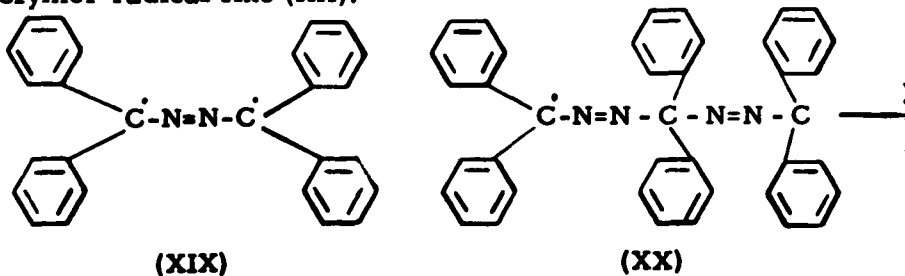


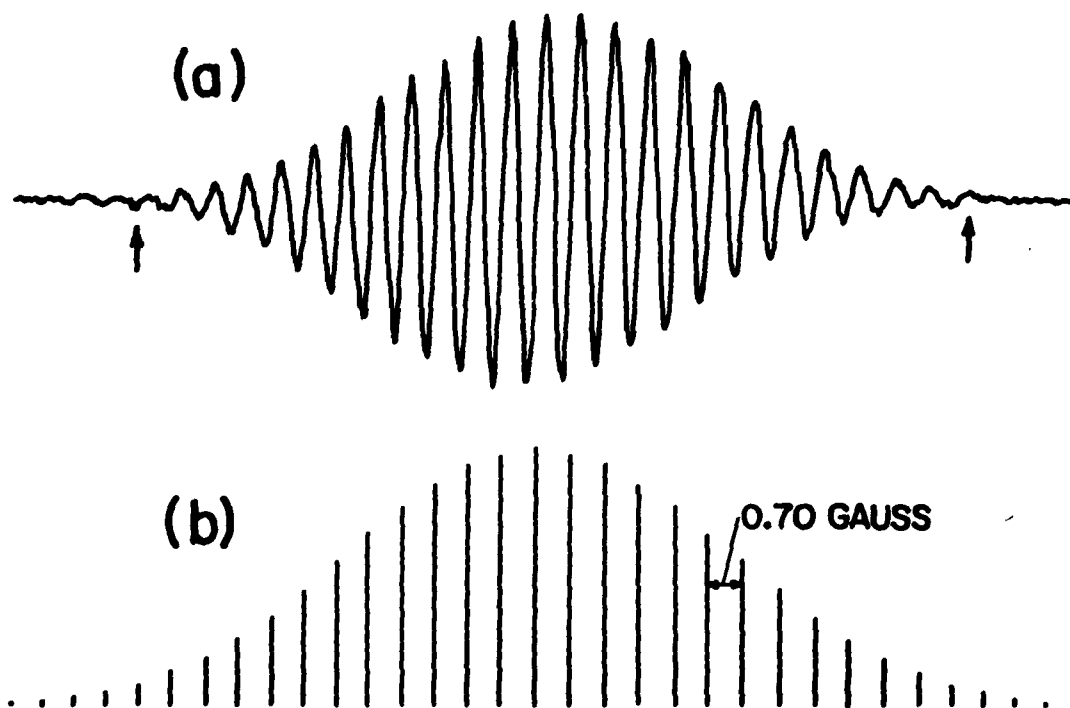
N-3504

Figure 11. Initial ESR Curve for a 1:20 Solution of Diphenyldiazomethane in m-Quinquephenyl at 140°C

These results indicate that there are two radical species involved. Since the long-lived radicals (Figure 12a) persist long after the red color of the starting diazo compound (XVII) has disappeared, they are believed to be intermediates in the conversion of the carbene to the azine end product. The short-lived radical (Figure 11) may be an intermediate in an earlier step of the reaction.

Possible intermediate radicals are the biradical (XIX) or a higher polymer radical like (XX).

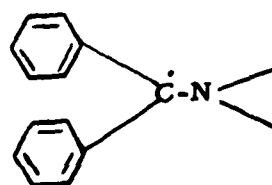




N-3542

Figure 12. (a) ESR Curve for Same Sample as in Figure 11 After 15 Minutes of Heating. (b) Line Spectrum Computed for Radical (XXI)

One can predict the ESR spectrum of a radical fragment such as (XXI),



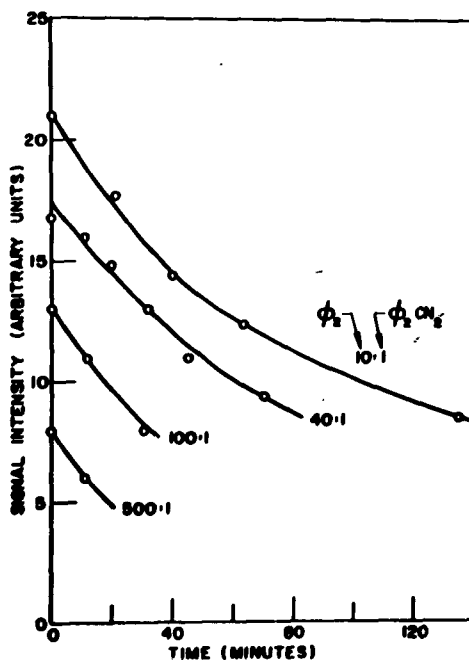
(XXI)

if the following reasonable assumptions are made:

1. The spin densities at the ring protons are $\rho_{\text{ortho}} = \rho_{\text{para}} = -2\rho_{\text{meta}}$. This relation has been found to be valid for a number of triphenyl methyl and biphenylaminium radicals of similar structure. ⁽¹⁵⁾ ⁽¹⁶⁾
2. The nitrogen splitting is equal to the smallest line separation, viz., 0.70 gauss, and to one-half the splitting produced by the meta protons.

The computed line spectrum is shown in Figure 12b. Although there is approximate agreement with experiment, there appears to be a discrepancy in the number of lines in the extreme wings. Any improvement in signal-to-noise will help determine the number of lines actually present in the experimental spectrum. Planned studies of analogous compounds with certain protons replaced by other substituents should also help remove the ambiguity in identifying the observed radicals.

One additional interesting ESR property of these radicals is the dependence of their concentration on dilution of the starting diazo compound in the inert solvent biphenyl. The results are shown in Figure 13. The maximum concentration of radicals in every case (10^{-4} to 10^{-5} molar) occurred a few minutes after inserting the sample into the preheated cavity. It is interesting to note that a change in concentration of 50 decreased the maximum radical concentration by only a factor of 3. The signals for all the samples were identical in width and shape to that in Figure 12a. Also note that the half-time for signal decay at 170°C was quite similar for all the samples, viz. about one hour.



N-3536

Figure 13. Diphenyldiazomethane in ϕ_2 at 170°C : Effect of Dilution and Decay of ESR Signal with Time

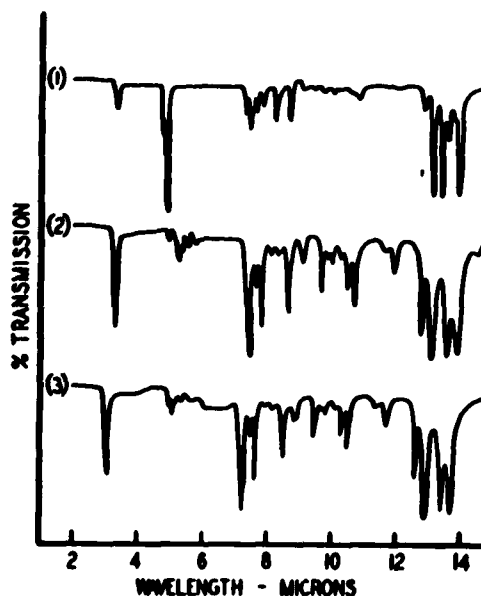
A reasonable explanation for these phenomena is that a polymer radical like (XX) dissociates into additional radicals, and that the fractional dissociation of polymer radical decreases with increasing dilution.

Both reversible and irreversible effects of small amounts of oxygen on the ESR were observed. Although the cause of these effects is not yet clear, it is obvious that considerable care must be taken in preparing "oxygen-free" samples.

5.2. Diazofluorene

The decomposition of the compound diazofluorene is of interest in connection with our investigations of the carbonization of fluorene derivatives. Unlike the diphenyl diazomethane, this material yields predominantly the dimer bifluorylidene on decomposition.

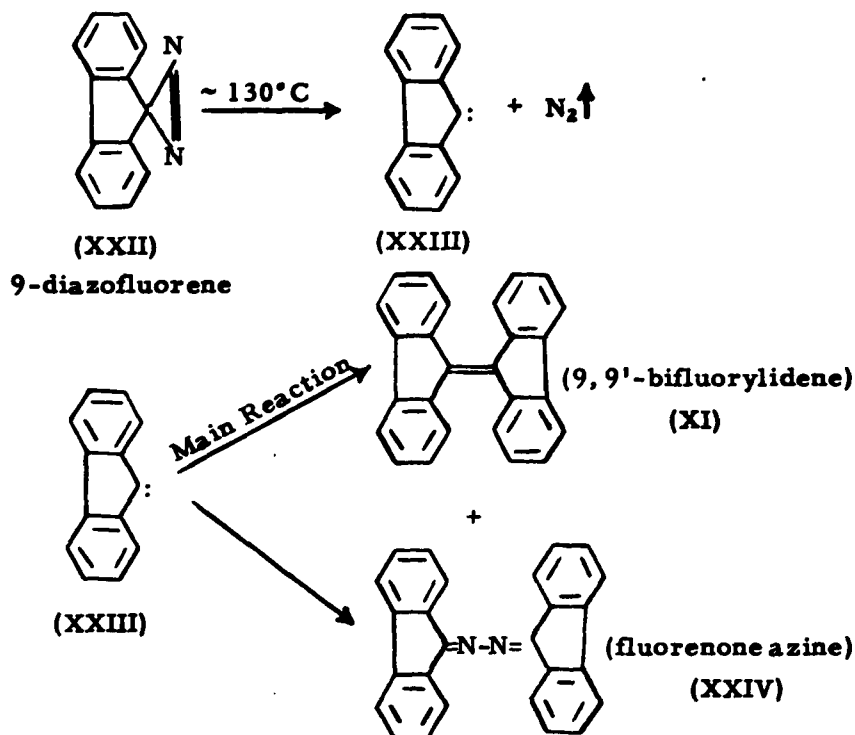
Shown in Figure 14 are the infrared spectra of the pure diazofluorene, the pyrolysis product at 130°C and that of pure 9,9'-bifluorylidene. It can be seen that the decomposition product is chiefly bifluorylidene. Careful extraction of this material, however, showed the presence of a nitrogen-containing component presumed to be the fluorenone azine (XXIV)



N-3978

Figure 14. Infrared Spectra for CS₂ Solutions of Diazofluorene and its Thermal Decomposition Products: (1) Diazofluorene, (2) Pyrolysis Product at 140°C, and (3) 9,9'-Bifluorylidene

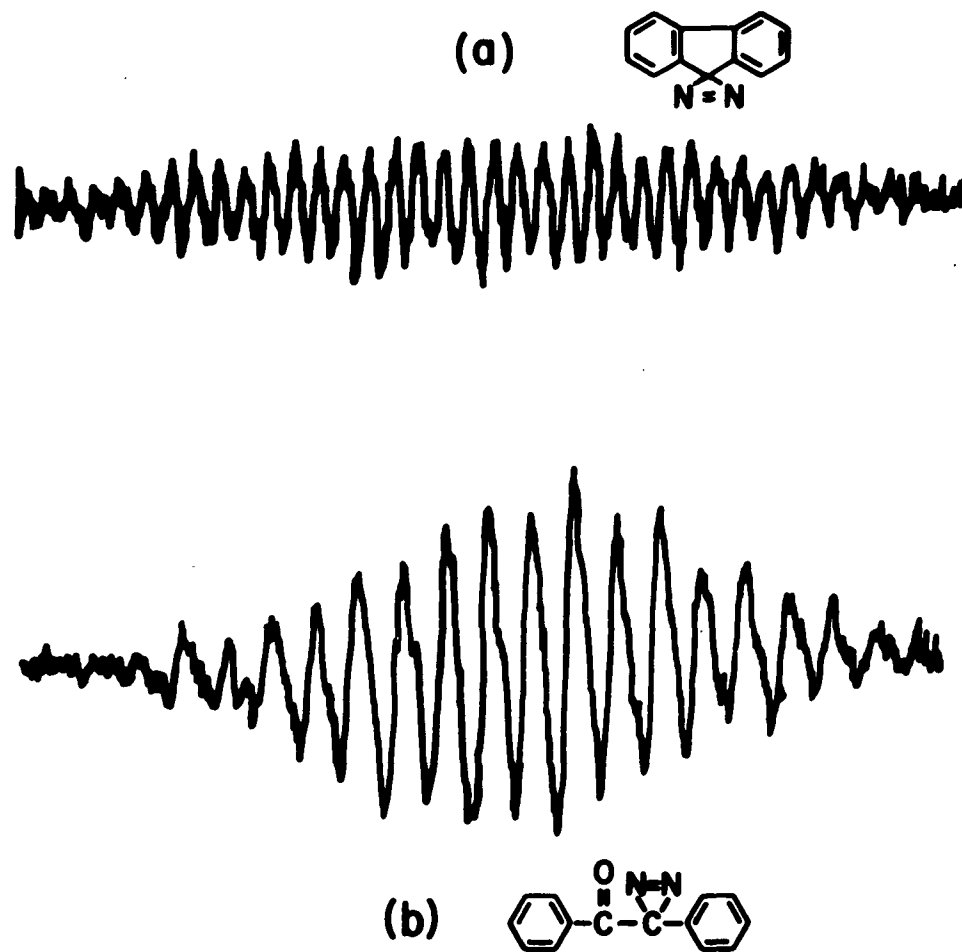
The reaction sequence can be outlined as follows:



An ESR curve for the radical intermediate in this decomposition is shown in Figure 15a. A substantial improvement in signal-to-noise will be required before an attempt is made to interpret the spectrum. Figure 15b also shows the ESR of the radical intermediate for decomposed diazo benzil.

6. CONCLUSIONS

We have shown that it is possible to carry out thermal decomposition and carbonization reactions in inert liquid solvents and to observe simultaneously the electron spin resonance properties. The observation of free radical intermediates in all the materials studied strongly suggests the general importance of free radical mechanisms in these processes. Well-resolved nuclear hyperfine structure in many of the resonance spectra provides unambiguous evidence for identifying the radical intermediates, and thus elucidating the mechanisms of chemical reaction. A detailed knowledge of these reactions will certainly clarify the relations between the microscopic structure of carbons and the nature of the starting materials.



N-3979

Figure 15. (a) ESR Curve for a 1:20 Solution of Diazofluorene in ϕ_2 at 140°C. (b) ESR Curve for a 1:20 Solution of Diazobenzil in ϕ_2 at 140°C

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<p>Aeronautical Systems Division, AF Materials Laboratory, Metals and Ceramics Division, Wright-Patterson AFB, Ohio.</p> <p>Rpt No. WADD-TR-61-72, Vol. XVI. RESEARCH AND DEVELOPMENT ON ADVANCED GRAPHITE MATERIALS: An Electron Spin Resonance Study of Thermal Decomposition Reactions of Organic Compounds. Final report, Jun 63, 24 p., incl. illus., table, 16 refs.</p> <p>Unclassified Report</p> <p>Initial results of an ESR (electron spin resonance) survey of the thermal decomposition and carbonization of pure organic compounds are presented. ESR measurements were performed during pyrolysis in inert polyphenyl solvents to permit the observation of</p> <p>(over)</p>	<ol style="list-style-type: none"> 1. Pure Organic Compounds 2. Electron Spin Resonance 3. Thermal Decomposition and Carbonization 4. Graphitization I. AFSC Projects 7350, 7381, 7-817, Tasks 735002, 738102 II. Contract No. AF 33(616)-6915 III. Nat'l. Carbon Co., Div. of Union Carbide Corp., Parma, Ohio IV. Singer, L.S., 	<p>Aeronautical Systems Division, AF Materials Laboratory, Metals and Ceramics Division, Wright-Patterson AFB, Ohio.</p> <p>Rpt No. WADD-TR-61-72, Vol. XVI. RESEARCH AND DEVELOPMENT ON ADVANCED GRAPHITE MATERIALS: An Electron Spin Resonance Study of Thermal Decomposition Reactions of Organic Compounds. Final report, Jun 63, 24 p., incl. illus., table, 16 refs.</p> <p>Unclassified Report</p> <p>Initial results of an ESR (electron spin resonance) survey of the thermal decomposition and carbonization of pure organic compounds are presented. ESR measurements were performed during pyrolysis in inert polyphenyl solvents to permit the observation of</p> <p>(over)</p>	<ol style="list-style-type: none"> 1. Pure Organic Compounds 2. Electron Spin Resonance 3. Thermal Decomposition and Carbonization 4. Graphitization I. AFSC Projects 7350, 7381, 7-817, Tasks 735002, 738102 II. Contract No. AF 33(616)-6915 III. Nat'l. Carbon Co., Div. of Union Carbide Corp., Parma, Ohio IV. Singer, L.S.,
<p>resolved hyperfine structure of radical intermediates. The generality of radical formation during carbonization is demonstrated. Detailed investigations have been made on the model aromatic hydrocarbons, acenaphthylene, 9, 9'-bifluorenyl and 9, 9'-bifluorylidene which provide examples of extremes in graphitization behavior. Resolved spectra for acenaphthylene and two deuterated analogs are compared. Possible structures for the observed radicals from both acenaphthylene and the bifluorenyl-bifluorylidene system are presented.</p> <p>ESR studies are also reported for the thermal decomposition of several aromatic diazo-compounds.</p>	<ol style="list-style-type: none"> V. Lewis, I. C. VI. Aval fr OTS VI. In ASTIA collection 	<p>resolved hyperfine structure of radical intermediates. The generality of radical formation during carbonization is demonstrated. Detailed investigations have been made on the model aromatic hydrocarbons, acenaphthylene, 9, 9'-bifluorenyl and 9, 9'-bifluorylidene which provide examples of extremes in graphitization behavior. Resolved spectra for acenaphthylene and two deuterated analogs are compared. Possible structures for the observed radicals from both acenaphthylene and the bifluorenyl-bifluorylidene system are presented.</p> <p>ESR studies are also reported for the thermal decomposition of several aromatic diazo-compounds.</p>	<ol style="list-style-type: none"> V. Lewis, I. C. VI. Aval fr OTS VI. In ASTIA collection